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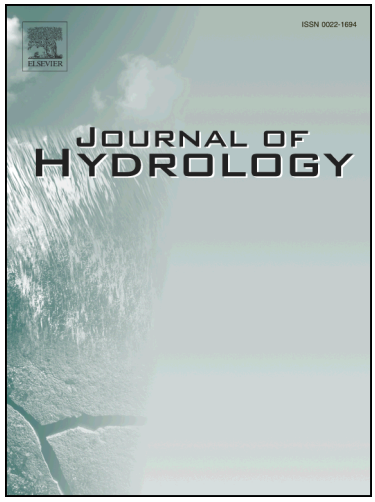

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The impact of moisture sources on the oxygen isotope composition of precipitation at a continental site in central Europe

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Abstract

The stable isotope composition of precipitation records processes taking place within the hydrological cycle. Potentially, moisture sources are important controls on the stable isotope composition of precipitation, but studies focused on this topic are still scarce. We studied the moisture

sources contributing to precipitation at Postojna (Slovenia) from 2009 to 2013. Back trajectory analyses were computed for the days with precipitation at Postojna. The moisture uptake locations were identified along these trajectories using standard hydrometeorological formulation. The moisture uptake locations were integrated in eight source regions to facilitate its comparison to the monthly oxygen isotope composition ($\delta^{18}O$ values) of precipitation. Nearly half of the precipitation originated from continental sources (recycled moisture), and more than 40 % was from central and western Mediterranean. Results show that moisture sources do not have a significant impact on the oxygen isotope composition at this site. We suggest that the large proportion of recycled moisture originated from transpiration rather than evaporation, which produced water vapour with less negative $\delta^{18}O$ values. Thus the difference between the oceanic and local vapour source was reduced, which prevented the distinction of the moisture sources based on their oxygen isotope signature. Nevertheless, $\delta^{18}O$ values of precipitation are partially controlled by climate parameters, which is of major importance for paleoclimate studies. We found that the main climate control on Postojna $\delta^{18}O$ values of precipitation is the surface temperature. Amount effect was not recorded at this site, and the winter North Atlantic Oscillation (NAO) does not impact the $\delta^{18}O$ values of precipitation. The Western Mediterranean Oscillation (WeMO) was correlated to oxygen stable isotope composition, although this atmospheric

pattern was not a control. Instead we found that the link to $\delta^{18}O$ values results from synoptic scenarios affecting WeMO index as well as temperature. Therefore, interpretation of $\delta^{18}O$ values of precipitation in terms of climate is limited to surface temperature, although at least half of the variability observed still depends on unknown controls of the hydrological cycle.

Keywords: Moisture sources; $\delta^{18}O$; Back trajectories; Transpiration; Slovenia

1. Introduction

Stable isotopes of precipitation record atmospheric process related to the hydrological cycle (Dansgaard, 1964; Rozanski et al., 1993; Gat, 1996; Araguás-Araguás et al., 2000; Gat et al., 2001; Darling et al., 2006; Sharp, 2007; Gat, 2010). A series of empirical correlations between certain parameters and water isotopes of precipitation ($\delta^{18}O$ and δD values) were described by Dansgaard (1964). In that early study, controls on the isotope composition of precipitation were called effects. Some of these effects were related to climate (i.e., temperature effect and amount of precipitation effect), establishing a connection between isotope ratios of precipitation and climate. The variability of isotope ratios in most continental

paleoclimate records largely depends on the variability of the isotope composition of precipitation (Leng, 2006). Thus, in continental archives, $\delta^{18}O$ or δD records have been used to reconstruct temperature (e.g., Pettit et al., 1999) or amount of precipitation (e.g., Wang et al., 2001). Additionally, the isotope composition of precipitation is affected by multiple atmospheric processes, and its variability can be used to trace different components of the hydrological cycle to better understand the controls on precipitation (Rozanski et al., 1982; Gat and Matsui, 1991; Risi, et al., 2008; Field et al., 2010).

In mid- and high-latitudes, mean monthly surface temperatures, typically measured 2 m above ground level, are statistically correlated with the monthly isotope composition of precipitation (Dansgaard, 1964). At these latitudes, the amount effect is commonly not a significant control, although there are important exceptions, especially in subtropical regions (e.g., Domínguez-Villar et al., 2008). The amount effect dominates the isotope composition of precipitation in tropical regions, where the temperature effect often vanishes (Rozanski et al., 1993). Climate modes of variability such as the North Atlantic Oscillation (NAO) are as well correlated with isotopes in precipitation (Baldini et al., 2008). This empirical relationship was confirmed using models (Field, 2010; Langebroek et al., 2011; Comas-Bru et al., 2016). In addition to temperature, amount of precipitation and

atmospheric circulation patterns, the source of moisture is considered an important control on the isotope composition of precipitation (Cole et al., 1999; Gat et al., 2001; Friedman et al., 2002; Cruz et al., 2005; Lachniet et al., 2009), and is often discussed in the interpretations of $\delta^{18}O$ and δD records (e.g., Aggarwal et al., 2004; Dayem et al., 2010; Domínguez-Villar et al., 2017). However, most continental paleoclimate studies still ignore the importance of the moisture source on the control of isotope composition of precipitation due to the complexity of its quantification, limiting the accuracy of interpretations. There are several methods to evaluate the role of moisture source in the isotope composition of precipitation.

The deuterium excess, also referred as "d-excess" or "d", was defined according to the equation: d-excess = $\delta D - 8 \cdot \delta^{18}O$ (Dansgaard, 1964). Early studies related d-excess to evaporative processes at the moisture source location (Craig and Gordon, 1965; Gat and Carmi, 1970). Thus, characteristic values of d-excess measured in precipitation were associated to particular regions of moisture uptake having distinct evaporative dynamics (Rindsberger et al., 1983; Cruz-San Julian et al., 1992; Celle-Jeaton et al., 2001). Therefore, this parameter was used to interpret variations in the moisture source regions or locations from paleorecords (e.g., Charles et al., 1994; Masson-Delmotte et al., 2005). When moisture

sources are mostly oceanic, sea surface temperature (SST) and relative humidity over the sea are major controls of d-excess (Johnsen et al., 1989). In regions such as Antarctica, where changes in relative humidity are limited, SST at the moisture source region dominates the d-excess variability (Vimeux et al., 1999; Uemura et al., 2012). Otherwise, relative humidity at the source region is responsible for most d-excess variability (Sharp, 2007;). However, rather than relative humidity, evaporation flux causes such variability (Pfahl and Sodemann, 2014), whereas not only relative humidity but wind speed can affect the d-excess. Distance to the coast was identified as a parameter affecting d-excess (Gat et al., 2003), providing additional controls that limit the identification of unambiguous ocean regions as moisture sources. On the other hand, when significant amount of moisture originated over the continents contributes to precipitation, the d-excess signal results from the mixture of moisture from both sources, and the oceanic signal is modified. Furthermore, some precipitation events are the result of moisture originated exclusively over the continents. Variables such as elevation, sub-cloud evaporation of raindrops, recycling of continental moisture or length of the trajectory path over land are major controls the d-excess in continental precipitation (Rozanski et al., 1982; Froehlich, et al., 2008; Goldsmith et al., 2017). Evaporation is a process that impacts d-excess values, whereas transpiration does not (Froelinch et al., 2008), introducing additional

variability to the d-excess values of the recycled moisture. The multiple controls governing the d-excess values, and the large variability of this parameter within most regions, prevents d-excess values to be used, in most cases, as a reliable proxy of source regions. As consequence of the multitude of controls affecting d-excess, this parameter is not a reliable proxy to identify the origin of air masses contributing to precipitation, especially in continental regions having significant moisture recycling.

The history of air masses can be calculated using regional/general circulation models (e.g., Numaguti, 1999; Gimeno et al., 2010) or back trajectory analyses based on Lagrangian methods (e.g., Stein et al., 2015). General circulation and Lagrangian models can also include modules to incorporate isotopes in precipitation (Hoffmann et al., 1998; Sturm, 2005; Schmidt et al., 2007; Sodemann et al., 2008a; Pfahl and Wernli, 2008). However, discrepancies between observed and modelled isotope values still are locally important (e.g., Langebroek et al., 2011). Other approach is to compare observed isotope data with modelled sources of moisture (e.g., Baldini et al., 2010). Atmospheric models that calculate back trajectories of air masses, and that are relatively easy to use by most scientists, have become popular in the last decade. This has triggered the number of studies comparing stable isotopes and the origin of air masses (e.g., Vreča et al., 2007; Sjostrom and Welker, 2009; Breitenbach et al., 2010; Abouelmagd et

al., 2012; Dumitru et al., 2017). However, the calculated air mass trajectories from a site during the days previous to the precipitation events do not provide the moisture sources of those precipitation events. Air masses do not uptake moisture along their full trajectory, but only when certain requirements are fulfilled (Sodemann et al., 2008b). Consequently, the spatial distributions of back trajectories and moisture uptake locations are very different. So, the use of back trajectories by itself is clearly insufficient and inadequate to identify moisture uptake locations. The calculation of moisture uptake locations using back trajectories requires running an additional model to identify locations of moisture sources (Sodemann et al., 2008a; Pfahl and Wernli, 2008; Baldini et al., 2010; Gao et al., 2011; Bershaw et al., 2012).

Previous studies have shown that, at least for some locations, moisture sources have a major control on the $\delta^{18}O$ values of precipitation, and that this control should be considered when interpreting paleoclimate from $\delta^{18}O$ records such as those from speleothems (Krklec and Domínguez-Villar, 2014). However, model studies suggest that atmospheric processes are capable to obliterate any original isotope signal of moisture sources (Field et al., 2010). Therefore, to know whether moisture sources have impact on the $\delta^{18}O$ values of precipitation at certain sites, local comparisons between these parameters are required. Here we use a

combination of Lagrangian back trajectory and hydro-meteorological models to calculate moisture sources of precipitation on a continental site of south central Europe: Postojna (Slovenia). Additionally, we have measured monthly $\delta^{18}O$ values of precipitation from Postojna during a 5-year period (2009-2013). The goal of this research is to evaluate whether the calculated moisture sources impact the oxygen isotope composition of precipitation at this site. Our motivation to study this location is to support the paleoenvironmental interpretation of $\delta^{18}O$ speleothem records from Postojna cave that are under construction. So, identifying controls affecting the $\delta^{18}O$ values of precipitation will contribute to a better understanding of processes affecting the hydrological cycle in the region.

2. Regional setting

This research is conducted in Postojna (45.78 °N; 14.20 °E), located in SW Slovenia (Fig. 1). The region is composed of carbonate rocks and characterised by numerous caves (Mihevc et al., 2010), the largest being the 20 km long Postojna Cave. Pisani Rov is a secluded side gallery of Postojna Cave where paleoclimate studies based on speleothem $\delta^{18}O$ records are being conducted (Domínguez-Villar et al., 2018). The meteorological station Postojna of the Slovenian Environment Agency (SEA) is located in the SW part of the town, 4 km apart from the studied

gallery (45°45'57'' N, 14°11'35''E, altitude 529 m). Postojna is in a topographic basin oriented WNW-ESE, surrounded by hills with average elevation around 800 m asl. Only two isolated peaks outstand from these hills (i.e., Mount Nanos, 1313 m asl, 13 km NW from the study site, and Javornik peak, 1268 m asl, 8 km SE from the study site). The Adriatic Sea is only 35 km to the SW and there is no major topographic barrier between the site and the closest coast of Adriatic Sea towards WSW. The topographical configuration of the region favours certain wind regimes, and the meteorological station of Postojna records predominant NNE winds (NMSS, 2017). Larger topographic barriers are already far from Postojna to influence local movement of air masses (e.g., Julian Alps with elevations >2500 m asl are 65 km away).

Postojna region has a continental climate, and during the normal period 1971-2000, the mean annual temperature was 8.7 °C and the annual amount of precipitation was 1584 mm (Table 1). During this period, the average temperature of the warmest month (July) was 18.1 °C and the average temperature of the coldest month (January) was 0.1 °C. The precipitation lacks a dry season or any clear seasonality, although often slightly higher amounts of precipitation are recorded in autumn (Fig. 2). Precipitation occurs often as snow from January to March and snow cover lasts for months in winter. The high amount of precipitation recorded in the

region is among the largest in southern Europe (excluding mountain regions) because the westerly winds provide moisture to the region from the proximal Adriatic Sea (Bolle, 2003). The inter-annual variability of precipitation during the normal period 1971-2000 was significant in Postojna (i.e., ±417 mm; 2 standard deviations). However, annual amount of precipitation was always above 1000 mm/yr. The potential evapotranspiration in Postojna during the reported normal period was 684.2 mm (SEA, 2017), with inter-annual variability (2 standard deviations) being 65.9 mm. These data clearly show that the region has a positive hydrological balance. This favourable hydrological balance, together with the land use planning, is responsible for the ample distribution of mixed forests (i.e., spruce, fir, beech and oak trees) over the region.

3. Methods

Precipitation for oxygen isotope analyses was collected by the SEA at the Postojna meteorological station. Hydrogen isotopes of precipitation were not considered in this study due to its limited application as an accurate proxy to identify moisture sources, as previously described. The outcome of this research will be used together with the results from a cave monitoring and modelling study (Domínguez-Villar et al., 2018) to better understand the controls on speleothem $\delta^{18}O$ records at this site. Therefore,

this research focuses exclusively on oxygen isotopes of precipitation. Precipitation (liquid or solid) was collected daily and transferred to a larger bottle that was replaced every month. These bottles were kept properly capped and stored in a basement without large temperature variations to prevent evaporation. Soon after collection, an aliquot was transferred from each bottle (i.e., those containing the water from monthly precipitation) to analytical vials that were stored in a fridge until their analysis in the laboratory. The $\delta^{18}O$ values of water samples were determined by equilibration with CO_2 for 12 hours at 25 °C (Epstein and Mayeda, 1953). The analyses were conducted using the IsoPrime continuous flow IRMS with Multiflow Bio equilibration unit at Jožef Stefan Institute (Slovenia). Isotope ratios were normalised with two working standards (MiliQ water and snow, calibrated versus VSMOW2 and VSLAP2) and USGS47 and USGS48 reference materials as controls. Results are reported as ‰ VSMOW. The uncertainty of these measurements is ±0.1 ‰, and was calculated in agreement with the method recommended by IAEA (Kragten, 1994).

To determine the source of moisture in precipitation over Postojna, we ran two different models. These models are: (1) reconstruction of air mass history (back trajectories) and (2) identification of the moisture uptake locations along reconstructed trajectories of the air masses. In the first model, we reconstructed 5-day trajectories of air masses prior to

precipitation using HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectories) trajectory model of the Air Resources Laboratory of the National Oceanic and Atmospheric Administration (Stein et al., 2015; Rolph et al., 2017). This model, based on the data generated by the Global Data Assimilation System (GDAS) was run for the days with significant precipitation (i.e., >1 mm; thereafter days with precipitation) for the period 2009-2013. "Days with less than 1 mm of precipitation account for less than 0.01% of the total amount of precipitation. By discarding those values we still account for 99.99% of the recorded precipitation amount and prevent eventual instrumental noise to be included in the moisture source dataset. Trajectories were computed 120 hours (5 days) back in time to avoid increase of uncertainty of trajectories with duration, but to be within 10 days, time period that is considered as average residence time of water vapour in the atmosphere (Numaguti, 1999). The air mass history was calculated for a single elevation over Postojna. Previous studies showed that the source of moisture at different elevations have a limited variation (Krklec and Domínguez-Villar, 2014). The elevation was chosen after comparing the results of calculated moisture sources at five different elevations for months January and July for 2009-2013 period: 500, 1000, 2000, 2500 and 3000 m agl (above ground level). Moisture sources were calculated after running the second model as explained below. Most of the moisture in the atmosphere is thought to be in

the first 2000 m agl (Wallance and Hobbs, 2006; Bershaw et al., 2012), so no higher levels were considered. The runs that provided more days with precipitation having identified moisture uptake locations were located at an elevation of 500 m agl. Topographic constraints are not a major limitation for air masses at this elevation (i.e., 1100 m asl). Therefore, all the analyses reported in the study are calculated for that elevation that is assumed to be representative of the column of air where most of the moisture is contained.

The second model uses hydrometeorological calculations to identify moisture uptake locations along the previously calculated trajectories. This model requires certain data that was already obtained during the back trajectory analyses: hourly atmospheric pressure, potential and environmental temperature, precipitation and relative humidity acquired. These data are used to calculate specific humidity using standard equations for saturation vapour pressure, saturation humidity mixing ratio, and specific humidity, consistent with Baldini et al. (2010). Following equations were used:

Saturation vapour pressure (e_s):

$$e_s = e_{so} \exp\left[\frac{L}{R_W T_0^2} T'\right]$$

Where:

At T' = 0, $e_s = e_{s0}$ = 6,1 hPa

L = latent heat of vaporisation of water (at 273.15 K = 0° C) = 2.5 x 10^6 Jkg^{-1}

R_w = specific gas constant for water vapour = 461 $Jkg^{-1}K^{-1}$

T_o = 273.15 K

T' = ambient temperature along a trajectory

Ratio of the molecular weights of water vapour to dry air (□):

$$\varepsilon = \frac{M_\omega}{M_d}$$

M□ = the molecular mass of water vapour = 18.02 x 10^{-3} kg mol^{-1}

Md = the molecular mass of dry air = 28.99 x 10^{-3} kg mol^{-1}

Saturation humidity mixing ratio (r_s):

$$r_s = \frac{\varepsilon e_s}{p - e_s}$$

Where:

p = atmospheric pressure (hPa) at the trajectory's vertical position above sea level; HYSPLIT output data

Specific humidity (q):

$$q = \frac{r_s}{1 + r_s} \times 1000$$

To calculate the moisture uptake (according to Sodemann et al., 2008b) we used specific humidity data, although we consider a more conservative threshold of positive gradient in specific humidity (0.5 g/kg within 6 hours), consistent with Krklec and Domínguez-Villar (2014) for atmospheric pressure above 900 hPa in agreement with Baldini et al. (2010). Thresholds used in this kind of studies usually vary from 0.1 to 0.5 g/kg within 6 hours (e.g. Crawford et al., 2013, Krklec and Domínguez-Villar, 2014; Tyler et al., 2016). However, Wang et al. (2017) showed that using similar range of thresholds does not impact obtained results. Moisture uptake locations were identified along each trajectory. We accounted the percentage of moisture uptake in every location for a certain period (e.g., month). The percentage of daily precipitation was weighed considering the amount of precipitation during that period. Afterwards, the percentage of daily precipitation was divided equally into the number of identified moisture uptake locations along each trajectory, and attributed to each single moisture uptake location. The moisture uptake locations were calculated for monthly, seasonal (three-monthly), yearly and 5-year intervals. Seasons were defined as follows: winter (January, February, March), spring (April, May, June), summer (July, August, September) and autumn (October, November, December). Following methodology of

Krklec and Domínguez-Villar (2014), a grid of 0.5x0.5 degrees was used for spatial computation of moisture uptake locations. Each cell of the grid integrates the percentage of moisture uptake accumulated during different events and/or moisture uptake locations within that cell for the time interval under consideration (e.g., months). The resulting model provides a map with discrete locations showing the percentage of moisture uptake contributing to Postojna precipitation.

To evaluate the impact of these moisture sources on the $\delta^{18}O$ signal of precipitation we divided the area in regions, a common methodology to evaluate the role of moisture sources on isotope composition of precipitation (Krklec and Domínguez-Villar, 2014; Hu and Dominguez, 2015). For a particular region, the moisture uptake percentage results of the sum of the percentages of all the locations within that region for the period under consideration (e.g., month). The time series calculated reports the percentage of moisture originated in different regions contributing to Postojna precipitation. Figure 1 shows the regions considered in this study: Atlantic (AT); western Mediterranean (wM); northern Europe (nE); southern Europe and west Africa (sE+wA); north-east Europe (neE); south-east Europe and east Africa (seE+eA); Northern Sea and Black Sea (NS+BS) and east Mediterranean (eM). Three criteria were considered when defining these regions: (1) geographical limits (e.g., ocean-continent

borders, major mountains, etc), (2) the distribution of moisture uptake locations (i.e., areas where our results show certain concentration of moisture uptake locations), (3) areas with relatively homogeneous $\delta^{18}O$ values (e.g., Schmidt, 1999; Bowen and Wilkinson, 2002). Moisture regions were correlated to monthly values of $\delta^{18}O$ values of precipitation. A correlation was considered statistically significant when p-values were <0.05. Additionally, we compared the oxygen isotope composition of precipitation to sea level pressure. We used re-analysis data from ERA-Interim and correlation maps were produced using KNMI Climate Explorer (KNMI, 2017).

4. Results

Climate parameters recorded during the period 2009-2013 in Postojna display higher temperatures than those recorded during the normal period 1971-2000 (Table 1). The observed difference is the result of a progressive warming trend started in the early 1980s representing the local expression of the global warming (e.g. Ogrin, 2004; Ogrin et al, 2011; De Luis et al.,2014; Domínguez-Villar et al., 2015). On the other hand, the amount of precipitation during the 2009-2013 period had minor differences when compared to the 1971-2000 normal period, which are not significant considering theinter-annual variability. Average number of days with

precipitation was essentially stationary. During the 5-year period of the study, we record a total of 552 days with precipitation. Back trajectories and moisture sources were calculated for all those days.

4.1. Back trajectories

The air mass history of the 5 days before every precipitation event over Postojna is displayed in Figure 3. The map shows a dense and scattered distribution of locations where the air masses passed over before reaching Postojna. Trajectories of air masses are highly represented in proximal zones such as the Mediterranean or Europe. The studied air masses often passed over the North Atlantic, northern Africa and Middle East, whereas they were less commonly found moving over the Arctic, North America, Greenland or Siberia. All trajectories were run for the same duration, and consequently, longer trajectories imply faster air flow. Stronger/dominant winds in Europe are from the west due to its latitudinal position (Barry and Chorley, 2003), causing the whole dataset of back trajectories being biased towards the west of the studied location. However, other wind regimes are also found in the region and air masses travelled thousands of kilometres in every direction before reaching Postojna. There is certain seasonal distribution of trajectories during different seasons (Fig. 4). During autumn and winter, when the gradient between Icelandic Low and Azores High is

increased (Bolle, 2003), we record longer trajectories over North Atlantic that even reach North America due to strong Westerlies. However, the air masses still arrive to Postojna from all cardinal points. During spring and summer westerly winds still represent a large proportion of the trajectories and back trajectories are still biased towards the west of the studied location. However, westerly trajectories are shorter in these seasons. No major differences are observed in trajectories from all other directions.

4.2. Moisture sources

The model identifies moisture uptake locations within the 120 hours previous to the precipitation event for >90 % of days with precipitation at Postojna. Majority of moisture contributing to Postojna precipitation originates in the Adriatic Sea, the Pannonian Basin and Po Valley (Fig. 5). Substantial amount of moisture is also originated in central Europe and in the western Mediterranean, but most distant locations such as the eastern North Atlantic are still important contributors. The uptake of moisture from northern Africa, eastern Europe, northern seas and Middle East have a limited contribution to Postojna precipitation. Large rivers in Europe such as the Danube are important sources of moisture to Postojna, too. On the contrary, elevated regions such as the Alps, the French Central System and the plateaus of Iberian Peninsula do not provide moisture to the studied

location. There are some seasonal differences in the locations of moisture uptake (Fig. 6). During winter and autumn most of the moisture is originated in the Adriatic and western Mediterranean, whereas central Europe sources have a limited contribution. African moisture contribution to Postojna precipitation is concentrated during these two seasons, and moisture uptake from Northern latitudes (i.e., 60 °N) was only recorded in autumn. During spring and summer, the moisture originated in central Europe increased substantially compared to other seasons, although still had a secondary role in comparison to Adriatic or western Mediterranean sources. Uptake of most moisture originated in the easternmost sources (e.g., 30 °E) took place only during spring.

Despite the reported map of moisture uptake is quantitative, in addition we divided the locations of moisture uptake in eight regions (Fig. 1). This division allows the calculation of a time series of cumulative percentage of moisture uptake for each region to facilitate further analyses. The average seasonal and annual distribution of moisture uptake for each selected region is provided in Table 2. It is worth noting that nearly half of the moisture contributing to Postojna precipitation is originated at the continents. This precipitation is known as recycled precipitation (e.g., Numaguti, 1999) and potentially has important impacts on the $\delta^{18}O$ values of precipitation (Salati et al., 1979).

4.3. Oxygen stable isotopes

The time series of $\delta^{18}O$ values of precipitation during 2009-2013 period is provided in Figure 7. The $\delta^{18}O$ values range from -2.8 to -13.1 ‰ with an average value of -7.7 ‰. The record of $\delta^{18}O$ values of precipitation shows seasonality with average amplitude in the order of 8 ‰, being the values more negative in winter than in summer. However, inter-monthly $\delta^{18}O$ variability is often high (i.e., up to 9.6 ‰). In the year 2011, this inter-month variability was so large that it disrupted the identification of the seasonal cycle. The average weighed annual $\delta^{18}O$ values of precipitation during the period 2009-2013 range between -7.4 and -9.3 ‰.

In the first analysis, we compared the monthly $\delta^{18}O$ values of precipitation and the integrated monthly moisture uptake in the eight defined regions. There is no significant correlation between any region and the $\delta^{18}O$ values of precipitation. The number of defined regions is subjective. Therefore, in the second analysis, we decided to merge some of the regions having similar geographical and isotope composition of their moisture sources (Schmidt, 1999; Bowen and Wilkinson, 2002). Results still showed no significant correlation. A third analysis was carried out splitting the sources only between continents (land) and oceans (sea). This analysis also resulted

in no significant correlation between moisture sources and $\delta^{18}O$ values of precipitation. Results of these analyses are summarized in Table 3.

5. Discussion

5.1. Moisture sources control on $\delta^{18}O$ values of precipitation

The $\delta^{18}O$ values of oceanic moisture sources that contribute to Postojna precipitation are expected to oscillate between -0.75 ‰ and +1.5 ‰ (Schmidt, 1999). High relative humidity in the ocean atmosphere justifies water vapour having a very limited wind dependent kinetic fractionation (Merlivat and Jouzel, 1979). Therefore, the oceanic water vapour isotope composition is assumed to be similar to that expected under phase change under isotopic equilibrium (Majoube, 1971). At the continents, moisture originates from diverse sources: (1) water contained in plants and other organisms, (2) soil water and (3) open water masses such as rivers, lakes or intercepted precipitation in impermeable surfaces (also known as canopy water). Examples of the latter occur when water is trapped on hollows or irregular surfaces of vegetation, as well as in temporary water ponds on rock or other impermeable substrates. Water vapour from plant transpiration does not have kinetic effects during fractionation compared to soil water (Bariac et al., 1991). However, metabolic processes in plants progressively fractionate the water content in the vegetal tissues from the

roots to the leaves, where transpiration eventually takes place (Bariac et al., 1994). On the other hand, water from soils and open water surfaces is subject to evaporation, which is a kinetic process due to the moisture deficit commonly recorded in the atmosphere at ground level. However, isotope models provide better results when very limited or negligible kinetic effects are associated to continental evaporation (Rozanski et al., 1982; Hoffmann et al., 2000). Isotope models consider evapotranspiration a sole process that occurs at equilibrium conditions (Sturm et al., 2010). This implies that the average water vapour of the atmosphere near the ground level in a continental site is expected to have an isotope composition very similar to a water vapour fractionated under equilibrium conditions with water having the average isotope composition of precipitation at that continental site. Thus, the oxygen isotope composition of the continental moisture sources of Postojna is expected to oscillate between -13.5 ‰ and -3.5 ‰ (Bowen and Wilkinson, 2002). Therefore, continents are more likely to be identified as a source region of moisture compared to oceans due to the large isotopic differences in comparison with various oceanic water masses (Krklec and Domínguez-Villar, 2014).

Our results show that in Postojna, the different sources of moisture do not impose particular signature on the oxygen isotope composition of precipitation that could be identified at significant statistical level. Despite

recycled precipitation accounts for nearly half of the precipitation in Postojna, none of the continental regions considered had a significant impact on the $\delta^{18}O$ values of precipitation. A study carried out on precipitation from Ljubljana, located only 40 km NE, proposed a model based on weather types that discerned the isotope composition of precipitation from different sources (Brenčič et al., 2015). Weather types indicate the origin of air masses, but not necessarily the source of moisture. In any case, the $\delta^{18}O$ values of precipitation associated by Brenčič et al. (2015) to different sources of moisture are mostly overlapping. Additionally, no test was conducted to evaluate whether the reported differences were statistically significant, or to evaluate the percentage of variance of the $\delta^{18}O$ values of precipitation explained by each moisture source. It is difficult to compare the results of both studies due to different methodologies. However, the similar $\delta^{18}O$ variability found studying different weather types is consistent with our results, pointing to a lack of impact of moisture sources on the $\delta^{18}O$ values of precipitation. Following the previous discussion, $\delta^{18}O$ value of continental moisture contributing to Postojna precipitation was expected to be more negative than the moisture from oceanic sources. Continental moisture accounts for nearly half the precipitation recorded in Postojna and it has significant seasonal and inter-annual variability.

Under these constraints, how is it possible that the original isotope signature of moisture sources does not provide a distinct isotope signature in precipitation? Postcondensation exchange between droplets and atmospheric vapour (i.e., sub-cloud processes) may erase any $\delta^{18}O$ signature from its original moisture source (Field, 2010). Postcondensation processes and moisture recycling modify the isotope composition of precipitation in relation to the otherwise dominant Rayleigh-distillation process (Rozanski et al., 1982; Koster et al., 1993; Field et al., 2010). Model studies assume that up to 80 % of droplets are re-evaporated (Sturm et al., 2010), and that the equilibrium between the droplets and the atmosphere vapour depends on the type of precipitation (Sturm et al., 2005). However, some regions clearly trace isotope anomalies recorded in source regions as shown, for example, in Greenland and Western Europe during the 8.2 ka event (LeGrande and Schmidt, 2008; Domínguez-Villar et al., 2009). How is then possible that some regions record distinct isotope signals depending on the moisture sources?

The isotope composition of water vapour originated from evaporation and transpiration can be estimated. Empirical and model studies confirm that water vapour originated by evaporation has in general at least 20 ‰ more negative $\delta^{18}O$ values compared to the water vapour originated from transpiration (e.g., Brunel et al., 1992; Wang and Yakir, 2000). These data

are consistent with Rayleigh distillation models from soil water subject to a limited evaporation (e.g., Gat, 1996). Therefore, the combination of variable amount of continental evaporation versus transpiration is an important contributor to the final isotope composition of water vapour in the atmosphere. Droplets of precipitation will mostly equilibrate with the water vapour of the atmosphere unless in case of convective precipitation. The isotope composition of water vapour measured over forests, where transpiration is enhanced, is several per mil less negative than the water vapour isotope composition measured over grasslands, where evaporation is favoured (Moreira et al., 1997; Tsujimura et al., 2007). Therefore, recycling of moisture originated from regions with high transpiration versus evaporation ratios will tend to decrease the differences in isotopic composition of moisture between oceanic and continental moisture sources. In Amazonia, where transpiration accounts for most of the moisture contributing to precipitation (Moreira et al., 1997), moisture recycling was not associated with more negative isotope ratios (Grootes et al., 1989). On the other hand, a study from the Iberian Peninsula, where there is a deficit in the hydrological balance and evaporation is a very important component of the hydrological cycle, Krklec and Domínguez-Villar (2014) found significant correlation between the recycled moisture from the Iberian Peninsula and stable isotope composition of precipitation. During spring and summer, precipitation from central Europe is expected to have less

negative $\delta^{18}O$ values than those expected from the temperature effect due to the increase of moisture recycling (mostly influenced in this region by transpiration), modifying the temperature effect gradient (Rozanski et al., 1982; Field et al., 2010). Recycling of moisture contributing to Postojna precipitation takes place mostly in central and eastern Europe, where hydrological balance is often positive (e.g., Wriedt and Bouraoui, 2009) and transpiration is enhanced versus precipitation (e.g., Granier et al., 2000; Domínguez-Villar et al., 2018). Soil water in temperate European sites have shown a limited impact of evaporation on the oxygen isotope signature (Comas-Bru and McDermott, 2015; Riechelmann et al., 2017). Therefore, we suggest that relative importance of transpiration versus evaporation is likely the cause of isotope signature of continental moisture sources not being differentiated from oceanic moisture sources contributing to precipitation in Postojna.

5.2. Climate information recorded in Postojna $\delta^{18}O$ values of precipitation

The record of oxygen isotope composition of precipitation has a seasonal cycle that is in phase with surface annual temperature (Fig. 8). Monthly $\delta^{18}O$ values of precipitation and temperature have a significant correlation (r^2=0.34; p-value<0.001). The relationship between monthly $\delta^{18}O$ values

of precipitation and amount of precipitation has a very weak, but significant correlation (r^2=0.07; p-value=0.04). When the relationship between amount of precipitation and $\delta^{18}O$ values is considered for individual years, none of them show a significant correlation. Anomalously, during the year 2011 the $\delta^{18}O$ values do not record a seasonal cycle. When this year is excluded from the analysis, the apparent amount effect during the 2009-2013 period becomes not significant (p-value=0.14) and the correlation with Postojna $\delta^{18}O$ values of precipitation and temperature is more robust (r^2=0.50; p-value<0.001). We consider that the apparent amount effect is just a statistical artefact caused by anomalous $\delta^{18}O$ values recorded during the year 2011. This is consistent with the lack of amount effect recorded in nearby (40 km) Ljubljana station (Vreča et al., 2005). Although $\delta^{18}O$ values of precipitation in Postojna are clearly impacted by temperature, at least 50 % of the isotope variability is not explained by this control.

Langebroek et al. (2011) suggested that rather than establishing a single climate parameter as control of the isotope ratios of precipitation, $\delta^{18}O$ values of precipitation should be related to atmospheric circulation patterns, since they integrate multiple components of climate. The dominant circulation mode in central Europe climate is the North Atlantic Oscillation (NAO). The oxygen isotope composition of precipitation in

several regions in Europe is related to the NAO index during winter months (Baldini et al., 2008; Field et al., 2010; Langebroek et al., 2011; Comas-Bru et al., 2016). During winter months, Postojna $\delta^{18}O$ values of precipitation and NAO index (Jones et al., 1997) are not correlated (r^2=0.02; p-value=0.526; DJFM months), and when the full year instead of the winter is considered, the correlation is not significant either (r^2=0.01; p-value=0.616). Mischel et al. (2015) found a relationship between winter NAO and cave drip water $\delta^{18}O$ values in Germany. This was possible because of infiltration of water to the epikarst occurred mostly during the winter season. However, in other sites where winter NAO has a strong influence on winter precipitation and $\delta^{18}O$ values of precipitation (Lamgebroek et al., 2011), speleothem $\delta^{18}O$ records are not related to the NAO record (Baker et al., 2011). This is due to mixing of water infiltrated during different seasons, a process that eventually eliminates the relationship between the isotope composition in the cave drip water and the NAO. In the studied gallery of Postojna Cave, the water is well mixed during the year, showing no seasonal bias (Domínguez-Villar et al., 2018). The latter is expected since precipitation is high every month (i.e., in average > 80 mm) and there is no seasonality (Fig. 2). Therefore, for climate variables to be recorded in the $\delta^{18}O$ signal of speleothems under investigation in Postojna Cave, the correlation of $\delta^{18}O$ values of

precipitation and climate variables should be significant during the full year.

Although NAO does not impact oxygen isotope composition of precipitation in Postojna, other atmospheric circulation patterns may be relevant. To investigate such possibility, we correlated Postojna monthly $\delta^{18}O$ values of precipitation with the sea level pressure from the ERA-Interim re-analysis database. The analysis shows different regions with significant correlation at 90 % confidence level (Fig. 9). The map shows a dipole with a pressure centre in between the tropical western Africa and the North Atlantic, whereas other pressure centre, having contrary correlation between sea level pressure and isotopes in precipitation, is located in northern Italy and the central Mediterranean. This pattern resembles the Western Mediterranean Oscillation or WeMO (Martín-Vide and López-Bustins, 2006). The WeMO is a pattern that involves the Azores High in the tropical North Atlantic and the Ligurian Low in the central Mediterranean during its positive phase, and a reverse pressure situation in those regions during its negative phase. Annual precipitation records from Slovenia are significantly correlated to WeMO index during the full year (Milošević et al., 2016). The $\delta^{18}O$ values of precipitation from Postojna have also a significant correlation with the WeMO index when data all over the year are included (r^2=0.13; p-value=0.005). We used a multivariate

regression analysis to correlate $\delta^{18}O$ values of precipitation with temperature and WeMO index to know if these two variables explain a larger percentage of the oxygen isotope variability of precipitation. The multivariate regression showed a significant correlation (r^2=0.34; p-value<0.001), although the model explained almost the same variability compared to the simple regression that correlated $\delta^{18}O$ values of precipitation and temperature. This is due to a significant correlation between temperature recorded at Postojna and the WeMO index (r^2=0.14; p-value=0.004). When the anomalous year 2011 year is eliminated from the dataset, the multivariate regression becomes identical to the simple regression that uses just temperature (r^2=0.50; p-value<0.001). Therefore, we consider that Postojna $\delta^{18}O$ values of precipitation represent a record of temperature. The correlation of $\delta^{18}O$ values of precipitation and WeMo index results mostly from similar synoptic scenarios, being the reason for WeMO pattern not explaining additional variability of the oxygen isotope composition of precipitation at Postojna.

Conclusions

We have evaluated the role of moisture sources in the oxygen isotope composition of precipitation at Postojna (Slovenia). At this site, $\delta^{18}O$ values of precipitation do not have particular signatures depending on the

sources of their moisture that we could identify at statistically significant levels. Despite recycling contributes moisture for nearly 50 % of the precipitation, and isotope of continental regions is significantly more negative than the moisture from oceanic sources, recycled precipitation does not show more negative $\delta^{18}O$ values. Previous studies have shown that water vapour originated from transpiration is much less negative than the vapour resulting from evaporation (Moreira et al., 1997; Wang and Yakir, 2000; Tsujimura et al., 2007). In continental regions, where recycling results mostly from transpiration, differences in the isotope composition of water vapour between continental and oceanic moisture sources is expected to be reduced. Therefore, in continental sites like Postojna, which recycled moisture originates in regions where the transpiration is more important than evaporation (i.e., central and eastern Europe), the limited difference between the oxygen isotope composition of the water vapour from different sources prevents the identification of moisture sources based on the $\delta^{18}O$ values of precipitation.

Postojna $\delta^{18}O$ values of precipitation are significantly correlated to surface temperature. We do not record amount effect, and the connection to some atmospheric circulation patterns (i.e., WeMO) is thought to be the response to similar synoptic conditions affecting temperature and that circulation pattern. Speleothems from Postojna Cave are under investigation and have

the potential to record a $\delta^{18}O$ signal related to the $\delta^{18}O$ values of precipitation. Therefore, these speleothems may be used to reconstruct temperature in the region. However, it should be kept in mind that certain percentage of the $\delta^{18}O$ variability may be related to unknown processes of the hydrological cycle.

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FIGURE CAPTIONS

Figure 1. Division of the eight regions where moisture uptake locations contributing to Postojna precipitation were identified. Regions are: Atlantic (AT), western Mediterranean (wM), northern Europe (nE), southern Europe and west Africa (sE+wA), north-east Europe (neE), south-east Europe and east Africa (seE+eA), Northern Sea and Black Sea (NS+BS) and east Mediterranean (eM). The star indicates Postojna location.

Figure 2. Average monthly amount of precipitation, evapotranspiration and temperature at Postojna meteorological station from 1971 to 2000.

Figure 3. Reconstruction of 5-day back trajectories previous to every day with precipitation at Postojna during the period 2009-2013. The star indicates Postojna location. The inset map shows the contours representing the frequency of calculated back trajectory positions during the full studied period per area (1x1 degree). To help visualization contours were depicted every 300 counts starting from 100 counts.

Figure 4. Seasonal distribution of 5-day back trajectories for days with precipitation at Postojna during the period 2009-2013. The star indicates Postojna location.

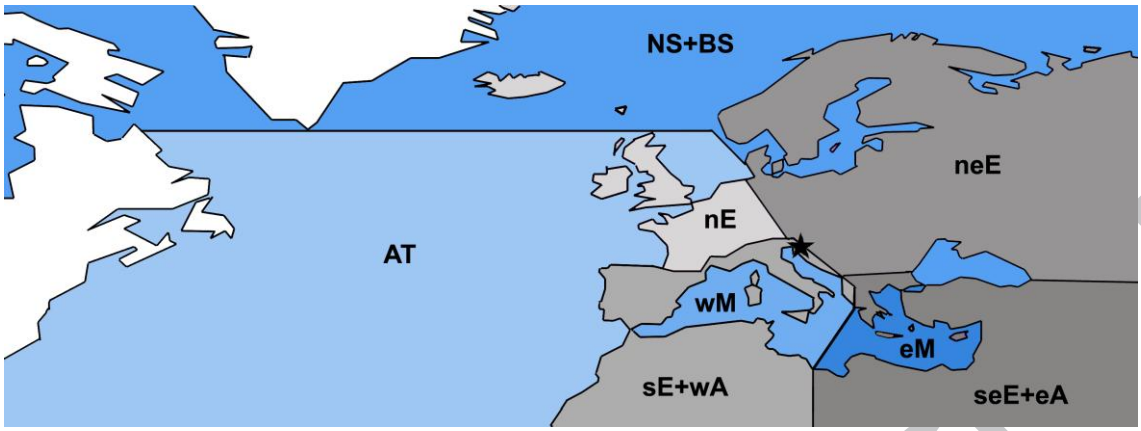
Figure 5. Moisture uptake locations contributing to Postojna precipitation during the period 2009-2013. Fill cells show moisture uptake at that location, whereas the colour indicates the proportion. The star indicates Postojna location.

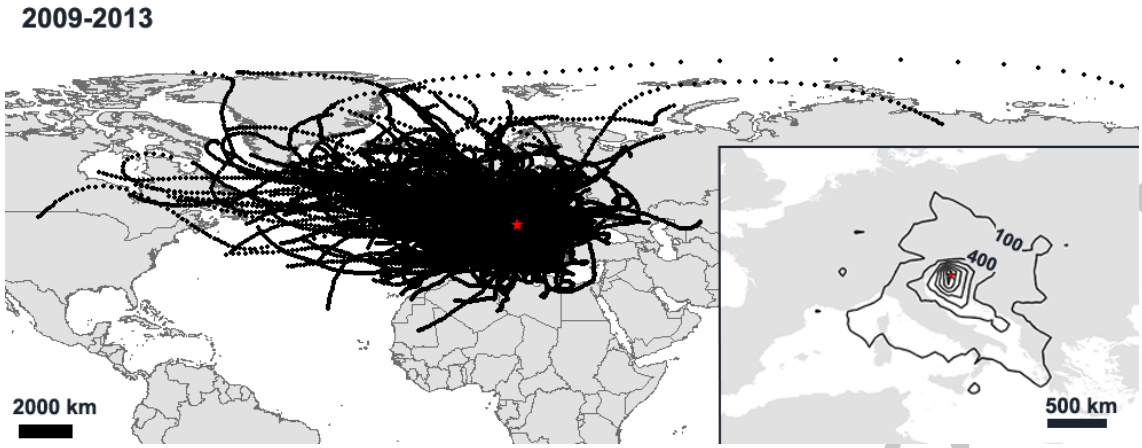
Figure 6. Seasonal distribution of moisture uptake locations contributing to Postojna precipitation. Fill cells show moisture uptake at that location, whereas the colour indicates the proportion. The stars indicate Postojna location

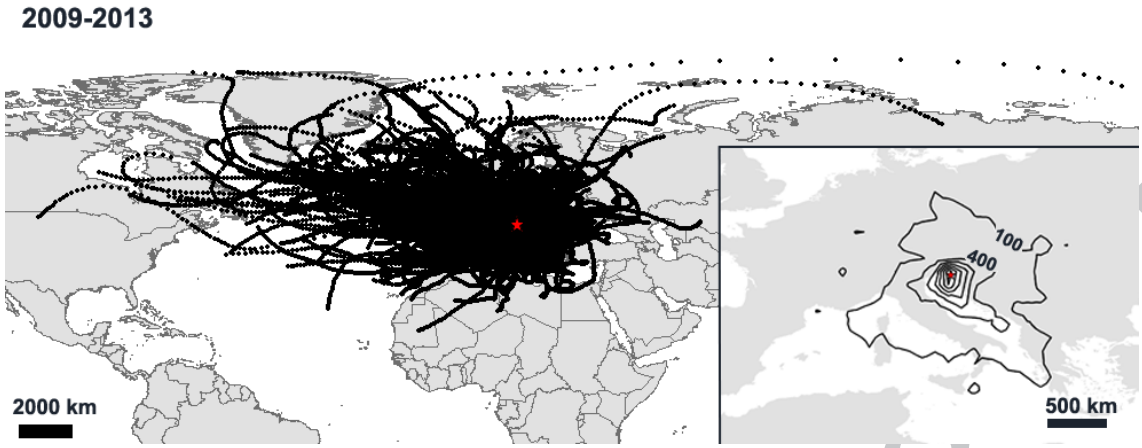
Figure 7. Time series of monthly $\delta^{18}O$ values of precipitation and the proportion of moisture from eight different regions contributing to Postojna precipitation from 2009 to 2013. Regions are: Atlantic (AT), western Mediterranean (wM), northern Europe (nE), southern Europe and west Africa (sE+wA), north-east Europe (neE), south-east Europe and east Africa (seE+eA), Northern Sea and Black Sea (NS+BS) and east Mediterranean (eM).

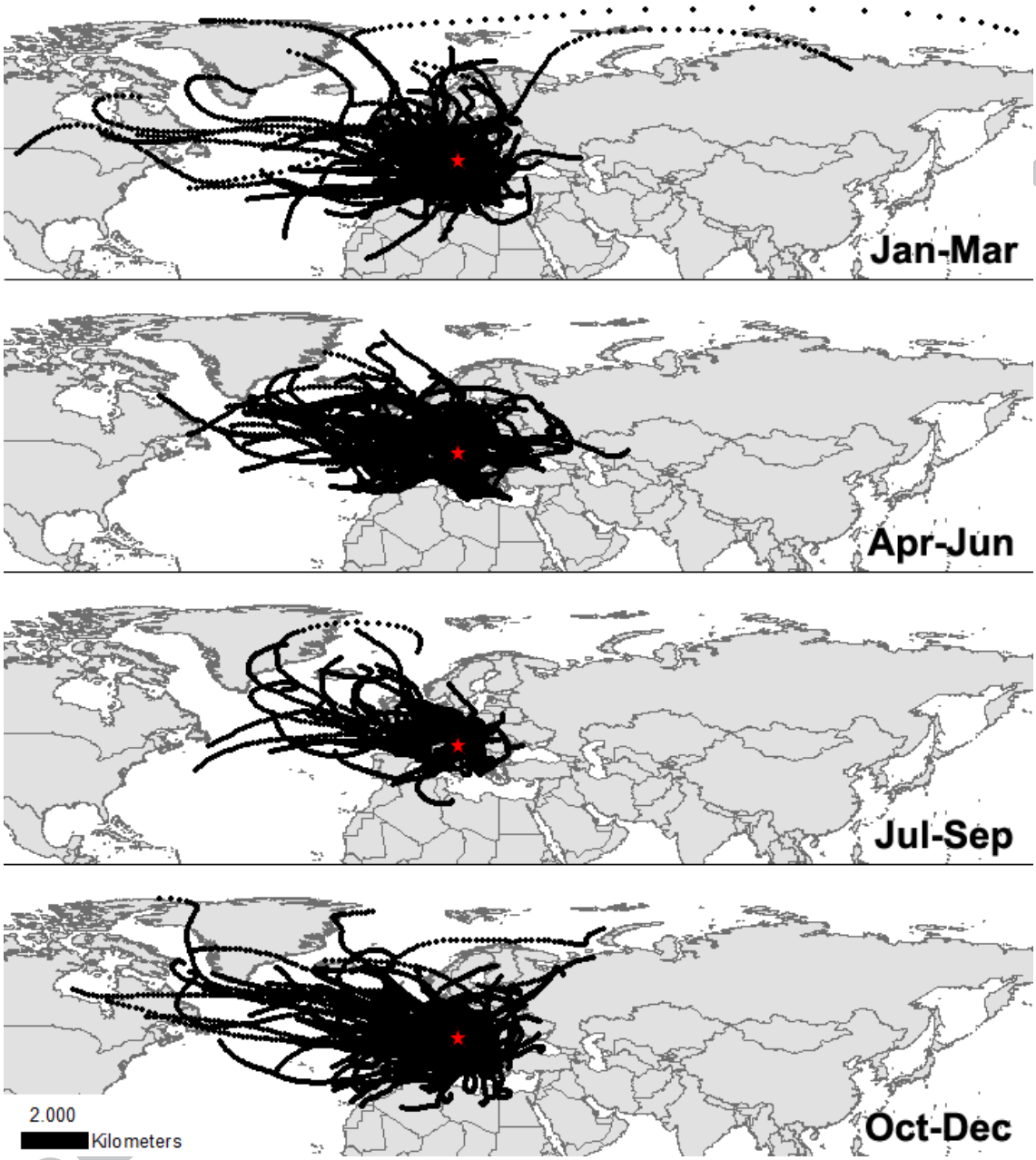
Figure 8. Time series of monthly $\delta^{18}O$ values of precipitation, amount of precipitation and temperature at Postojna from 2009 to 2013.

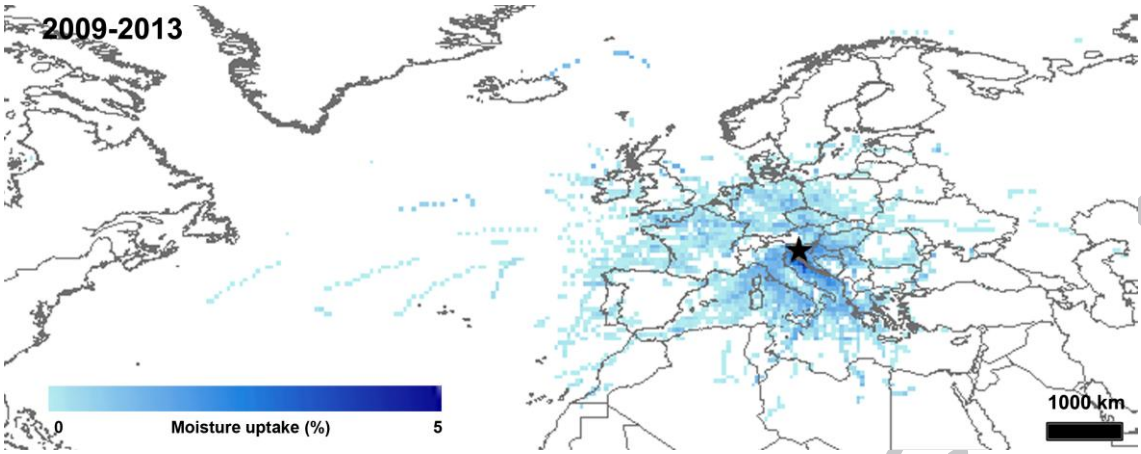
Figure 9. Correlation map of pressure fields at sea level from ERA-Iterim re-analysis database and monthly $\delta^{18}O$ values of precipitation in Postojna. Note the dipole between central Mediterranean and tropical Africa-North Atlantic region that resembles the Western Mediterranean Oscillation pattern.

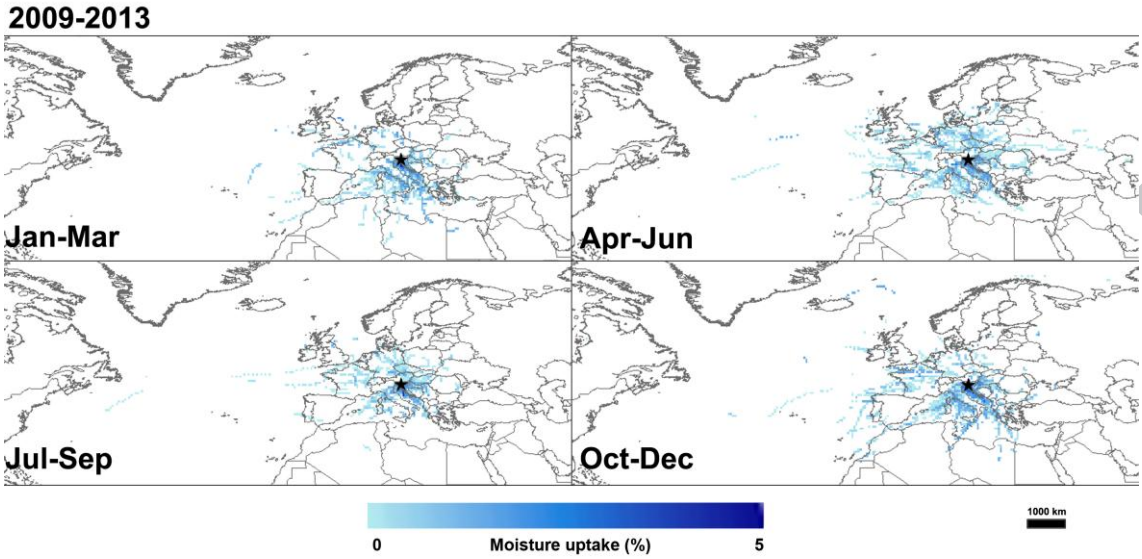


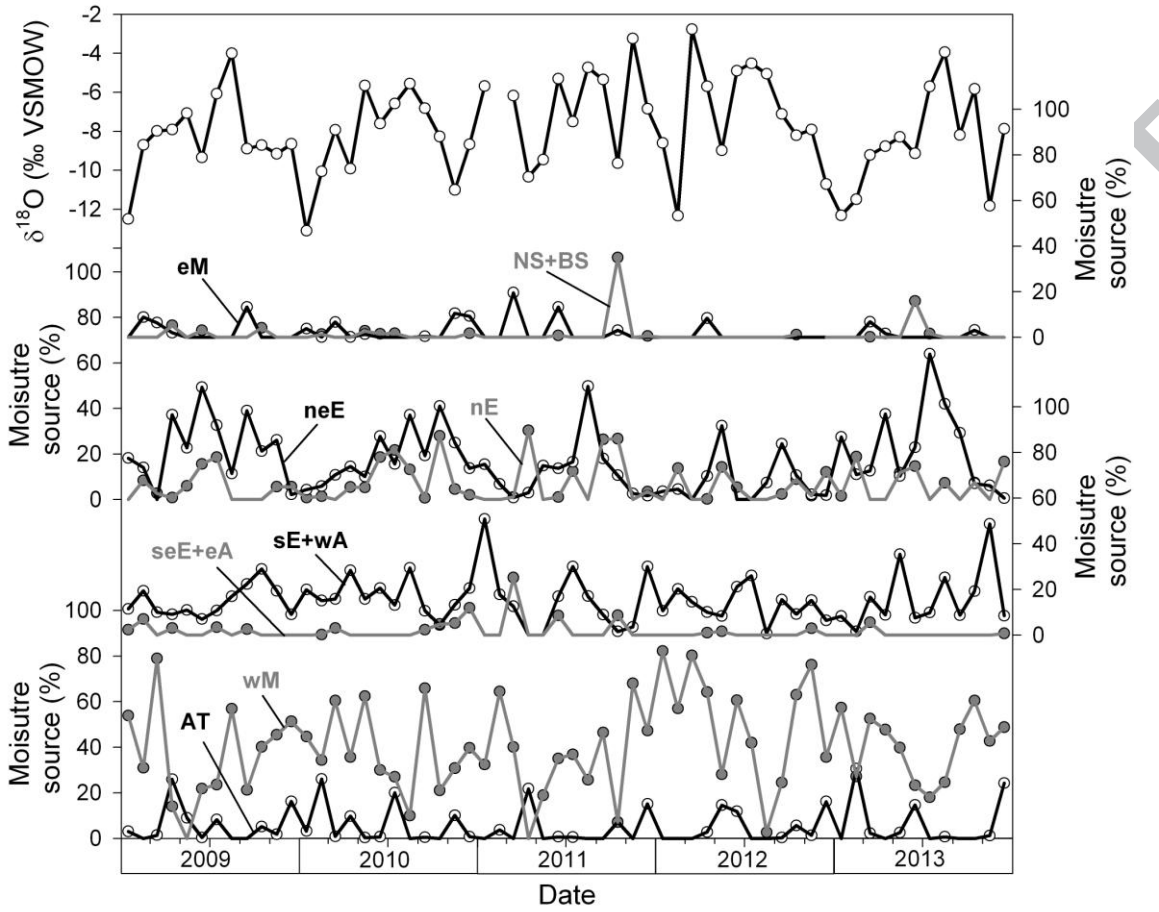


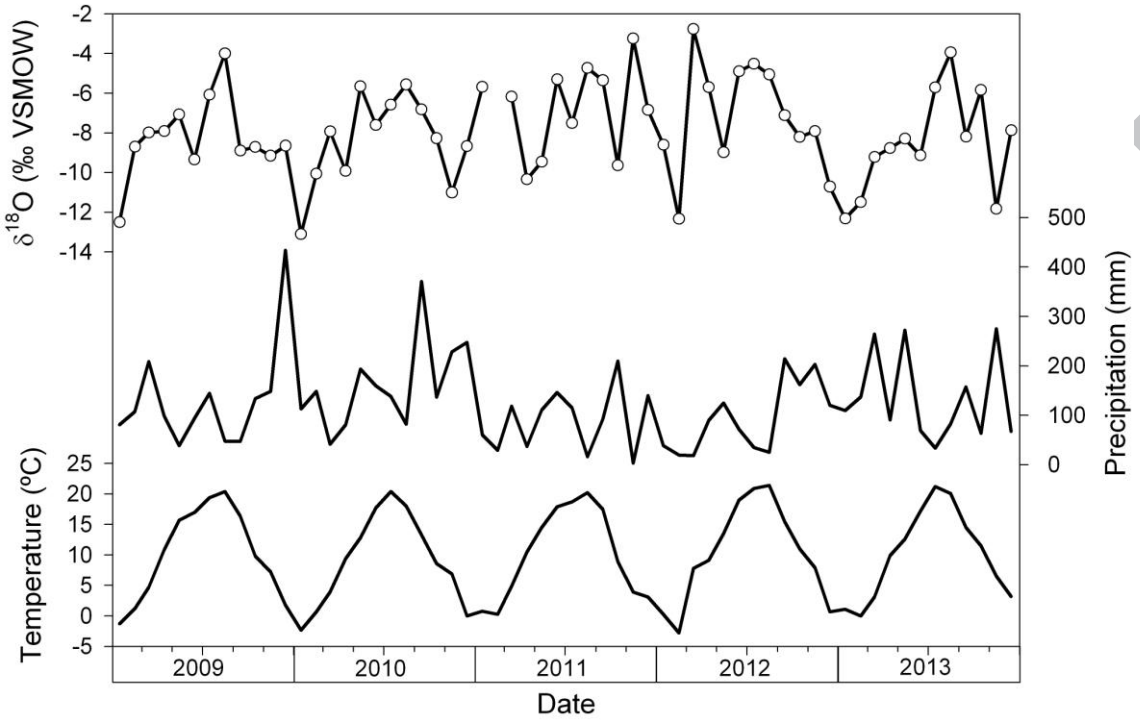












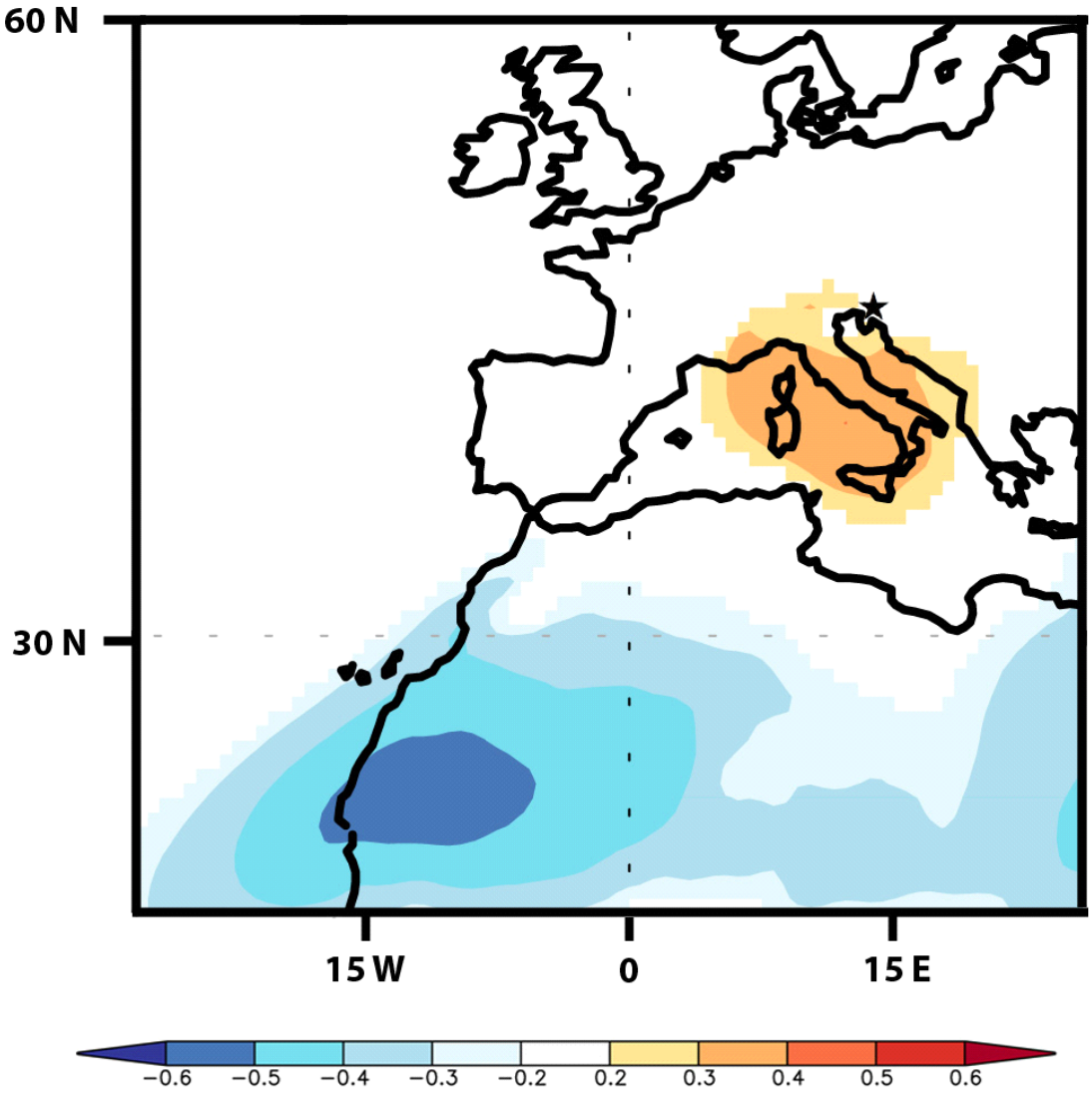


Table 1. Temperature, amount of precipitation and number of days with precipitation during the period 2009-2013 compared to the normal period 1971-2000.

	Mean annual T (°C)	Mean January T (°C)	Mean July T (°C)	Annual amount of precipitation (mm)	No. of days with precipitation
2009	10.3	-1.3	19.4	1582	114
2010	9.1	-2.3	20.4	1940	139
2011	10.1	0.8	18.7	1078	78
2012	10.4	0.3	20.9	1124	87
2013	10.1	1.1	21.2	1622	134
2009-2013	10.0 ±1.0	-0.3 ±2.9	20.1 ±2.1	1469 ±728	110 ±55
1971-2000	8.7 ±1.3	0.1 ±2.0	18.1 ±1.2	1584 ±417	111 ±21

Table 2. Percentage of integrated seasonal moisture uptake by seasons during the 2009–2013 period. Source regions are: Atlantic (AT); western Mediterranean (wM); northern Europe (nE); southern Europe and west Africa (sE+wA); north-east Europe (neE); south-east Europe and east Africa (seE+eA); Northern Sea and Black Sea (NS+BS) and east Mediterranean (eM).

Source region	Winter	Spring	Summer	Autumn	Annual
AT	6.48	5.61	2.73	7.50	6.58
wM	50.07	36.22	38.50	43.42	42.05
nE	3.27	8.33	7.81	7.58	6.98
sE+wA	14.71	16.47	15.09	17.17	16.04
neE	9.61	19.85	24.86	11.45	15.88
seE+eA	3.73	1.16	0.64	2.65	2.16
NS+BS	0.16	1.62	0.19	3.33	0.84
eM	4.56	1.90	0.49	2.14	2.26
TPIMS*	92.59	91.16	90.31	95.25	92.78

*TPIMS: Total percentage of identified moisture sources

Table 3. Correlation coefficients and p-values found between monthly proportion of precipitation which moisture was originated in different source regions and monthly $\delta^{18}O$ values of precipitation at Postojna. Source regions are: Atlantic (AT); western Mediterranean (wM); northern Europe (nE); southern Europe and west Africa (sE+wA); north-east Europe (neE); south-east Europe and east Africa (seE+eA); Northern Sea and Black Sea (NS+BS) and east Mediterranean (eM).

Source region	AT	wM	nE	sE+wA	neE	seE+eA	NS+BS	eM
p-Value	0.16	0.57	0.65	0.81	0.21	0.32	0.25	0.35
r^2	0.05	0.01	0.01	0.00	0.03	0.06	0.11	0.05

Source region	AT + NS+BS	wM+eM	sE+wA + seE+eA	nE+neE
p-Value	0.14	0.60	0.84	0.63
r^2	0.06	0.01	0.00	0.00

Source region	Sea	Land
p-Value	0.70	0.89
r^2	0.00	0.00

Highlights

Moisture sources of precipitation were calculated in central Europe during 2009-2013.
The impact of moisture sources on $\delta^{18}O$ composition of precipitation was quantified.
Moisture sources do not contribute significantly to the $\delta^{18}O$ values of precipitation.
The $\delta^{18}O$ variability is dominated by temperature.